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CRYSTALLIZATION CAPACITY OF $ZnB_2O_4 - NaPO_3$ GLASSES

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The crystallization capacity of glasses based on the system $ZnB_2O_4 - NaPO_3$ is investigated. The results of differential-thermal analysis, polythermic analysis, and x-ray phase analysis are described, making it possible to identify the crystallization intervals and the dependence of crystallization on the temperature-time factor.

The current development of new glass compositions for glass-ceramic materials in Russia and the CIS countries is insignificant and yet the demand for these materials is growing. The increased demand for universal materials capable of withstanding sharp destructive impacts and acting as vitreous binders in abrasive tools promotes synthesis of new materials with high mechanical parameters capable of replacing costly and less technologically suitable ceramic analogs.

The majority of known vitreous binders are created on the basis of silicates. When they are used as devitrifying binders for electrocorundum, a lithium-aluminosilicate phase with a low or negative TCLE is formed under firing in the abrasive – glass-ceramic boundary layer, which leads to disintegration of the material obtained. It is known that a stable glass cannot be obtained in the system of typical glass-forming oxides $B_2O_3 - P_2O_5$. Consequently, the study of the crystallization regularities and properties of glasses in the simplest borophosphate systems has not only theoretical but practical interest as well. This has motivated the research of glasses in the $ZnB_2O_4 - NaPO_3$ system that has a low melting temperature, good wettability of electrocorundum, and a relatively low TCLE (of the order of $50 \times 10^{-7} - 60 \times 10^{-7}\ K^{-1}$). The replacement of current vitreous binders by glass-ceramic binders of higher mechanical strength is a promising direction in the sphere of application of devitrifying materials.

The purpose of the present study is the development of new glass compositions for glass ceramics based on zinc metaborate.

Glasses based on ZnB_2O_4 were produced in glass-carbon crucibles. The maximum heating temperature was 1000 – 1100°C with an exposure of 35 – 45 min. Casting was performed in heated graphite molds with subsequent annealing in an electric muffle.

The density of the samples was measured by hydrostatic weighing. on an analytical scale with an accuracy of ± 0.2 mg.

The chemical composition of the main crystalline phase was determined using qualitative x-ray phase analysis on a DRON-2 set with CuK_α radiation.

The crystallization capacity of synthesized glasses was studied by the polythermic method that involved their heating in a gradient furnace in chamotte boats with the temperature varying from 500 to 900°C.

To determine the temperature and intensity of the crystallization process in the glasses obtained, differential-thermal analysis was performed in quartz crucibles up to a temperature of 1000°C using a Paulik – Paulik – Erdey derivatograph produced by MOM (Hungary).

The TCLE and the temperatures of vitrification and the start of deformation of glasses and glass ceramics were measured using a DKV-4 vertical quartz dilatometer in a temperature interval of 20 – 600°C using the standard method.

Table 1 lists the compositions of the synthesized glasses and the main results of studying the $ZnB_2O_4 - NaPO_3$ system.

The studies indicate that this system has two glass-formation ranges: the first one with $NaPO_3$ content ranging from 0 to 30%[2] and the second one with $NaPO_3$ content varying from 60 to 80%.

The glass containing 33% $NaPO_3$ is opalescent. Its crystallization capacity has the following general direction: as the phosphate component increases, the glass-melting temperature decreases. Furthermore, all glasses synthesized are capable of crystallization; however, its ranges are individual for each particular glass.

The derivatograms of all the glasses considered have exothermic effects indicating structural modifications occurring in the glass in releasing heat; in our case these are the crystallization processes (Fig. 1). For further study glasses

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[2] Here and elsewhere molar content.

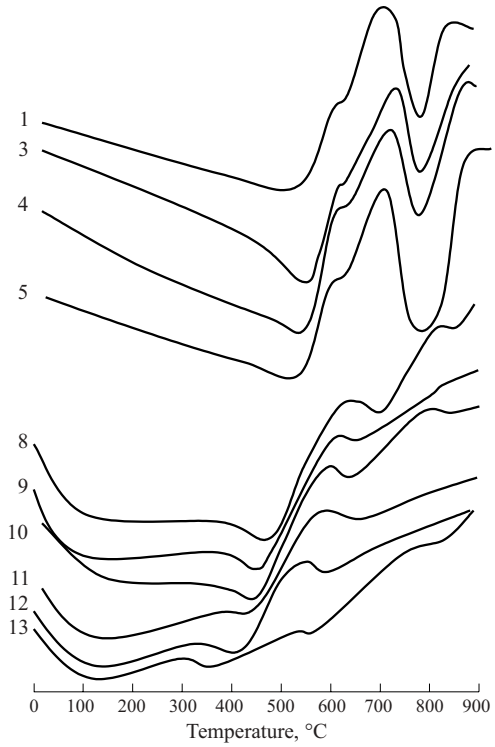

Fig. 1. DTA curves of borophosphate glasses. Curve numbers correspond to composition numbers.

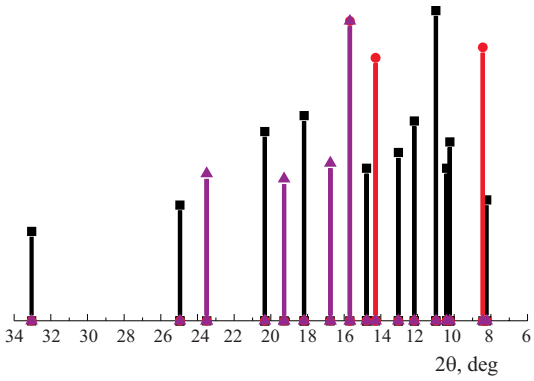

Fig. 2. X-ray diffraction diagram of borophosphate glass: ●) zinc borate $5ZnO \cdot 2B_2O_3$; ▲) zinc borate $ZnO \cdot 2B_2O_3$; ■) boron orthophosphate BPO_4.

with the maximum volume crystallization were selected. Based on DTA, dilatometric, and polythermic study data, heat treatment temperature intervals for production of glass ceramics materials were identified. An initial glass composition containing 20% $NaPO_3$ with a 10% $AlPO_4$ additive (above 100%) was used to obtain a material crystallized in its entire volume. The parameters of melt spreading over electrocorundum were determined for the glass with 30% $NaPO_3$. The spreading temperature was 825°C. The composition was subjected to two-stage thermal treatment, as a consequence of which a glass ceramic material was produced that adhered well to the corundum substrate. The x-ray phase analysis of the glasses of the system $ZnB_2O_4 - NaPO_3$ shows that the main crystallizing phases are BPO_4 and zinc borates (Fig. 2).

It is known [1 – 4] that some properties (density, TCLE, etc.) of glasses of the sodium-borate system vary discontinuously. The extremum corresponds to glass with approximately 18% Na_2O.

It was logical to expect that a similar dependence of the properties on the composition would be observed in glasses of the system $ZnB_2O_4 - NaPO_3$. The latter was experimentally corroborated (Fig. 3). It can be seen that with 40 and 80% $NaPO_3$ the curves of the dependence of the TCLE and density on the composition have inflections typical of borates. For reliability of the results obtained, measurements were performed on 4 – 5 samples of the same composition.

TABLE 1

Glass	Molar content, %		Density, g/cm^3	TCLE, 10^{-7} K^{-1}	Vitrification temperature, °C	Visual characteristics of glass
	$NaPO_3$	ZnB_2O_4				
1	0	100	3.359	50	545	Clear, transparent
2	1	99	3.351	51	540	The same
3	10	90	3.282	57	525	〃
4	20	80	3.168	65	522	〃
5	30	70	3.060	79	491	〃
6	33	67	3.000	85	470	Opalescent
7	35	65	2.987	92	451	Milky, surface crystallization
8	40	60	2.981	101	433	Milky, volume crystallization
9	50	50	2.959	106	428	The same
10	60	40	2.920	123	423	Clear, transparent
11	70	30	2.860	134	418	The same
12	80	20	2.797	145	380	〃
13	90	10	2.658	198	340	Milky, crystallization
14*	100	0	2.480	220	270	The same

* The data are taken from the reference book due to very intense crystallization of this glass.

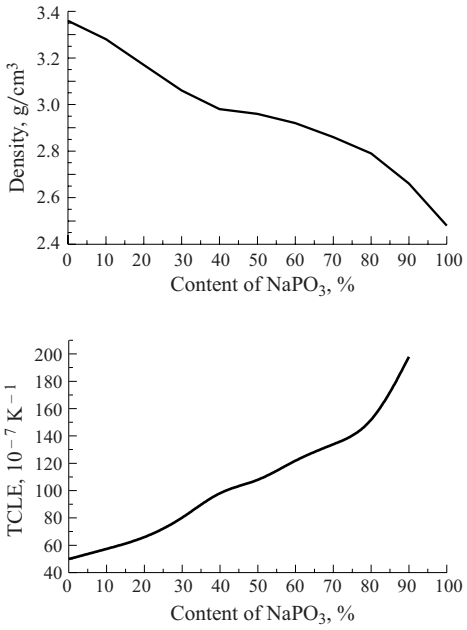

Fig. 3. Dependence of density (*a*) and TCLE (*b*) of glasses of the ZnB_2O_4 – $NaPO_3$ system on the molar content of $NaPO_3$.

The study of the NMR spectra of isotopes ^{11}B and ^{10}B based on published data [5 – 7] established that all boron in vitreous B_2O_3 exists in a trigonal environment, whereas oxygen introduced with alkali oxide (0 – 16% Na_2O) raises the share of four-coordination boron.

$$N_4 = \frac{x}{1-x}, \qquad (1)$$

where x is the molar part of the alkali oxide [5].

Furthermore, with the ratio

$$\frac{Me_2O + MeO}{B_2O_3} = \frac{1}{3} \qquad (2)$$

conditions for transformation of boron from the trigonal coordination to the tetragonal oxygen coordination [6, 7] are developed.

When conditions (1) and (2) are satisfied, the stoichiometric composition of glasses with the $NaPO_3$ content below 40% indicates the predominant role of B_2O_3 as the glass-forming agent, in which sodium and zinc oxides are "dissolved." The phosphate component in this case acts as a crystallization catalyst. The glasses in this range are clear and glasses with the content $30 < NaPO_3 < 33\%$ are opalescent. With 40 – 80% sodium metaphosphate, spontaneous crystallization takes place. This phenomenon is unstable and to a great extent depends on the conditions of melting. Thus, with $NaPO_3$ content above 80%, another change in the dominant occurs: a high-phosphate glass-formation range is here observed, whereas a ZnB_2O_4 additive decreases the propensity of the glass melt for spontaneous stratification, and therefore the glasses within this concentration range are opaque. Consequently, the jumps in property variations with increasing alkali-phosphate component are caused by the change of the matrix and the ensuing coordination transformation of boron.

Thus, two glass-formation ranges are identified in the ZnB_2O_4 – $NaPO_3$ system. As the quantitative ratio between ZnB_2O_3 and $NaPO_3$ changes, the glass-former matrix is replaced. Glasses of this system have a tendency toward catalyzed volume crystallization.

The devitrified glass obtained has good adhesion to electrocorundum, which makes it suitable as a basis for the production of a devitrifying binder for abrasive materials.

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